Rotationally resolved spectroscopy of jet-cooled NbMo

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Rotationally resolved resonant two-photon ionization spectra of jet-cooled NbMo are reported for the first time. A vibronic spectrum of NbMo was recorded in the 17 300–22 300 cm^{-1} spectral region. Although the observed bands could not be grouped into electronic band systems, four excited vibronic levels with $\Omega=2.5$ and two excited levels with $\Omega=3.5$ were identified. The ground state of NbMo has been assigned as $^2\Delta_{5/2}$, deriving from a $1\sigma^2 1\pi^4 1\delta^3 2\sigma^2$ configuration of the valence electrons. Rotational analysis of six bands provides a ground state rotational constant of $B_0''=0.087\,697(26)$ cm^{-1}, corresponding to a bond length of $r_0''=2.008\,09(30)$ Å for $^{93}Nb^{98}Mo$. Correction for the effects of the spin-uncoupling operator changes the estimated bond length only slightly to $r_0''=2.008\,02(30)$ Å. The experimentally determined value of r_0'' is compared to that predicted using previously determined multiple bonding radii of Nb and Mo. A comparison to the known diatomic molecules composed of group V and VI metal atoms is also made. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2778681]

I. INTRODUCTION

Resonant two-photon ionization (R2PI) experiments conducted in this laboratory during the past several years have provided gas phase spectroscopic data pertaining to the group V-VI intermetallics VCr,[1] NbCr,[1] and most recently, VMo.[2] These investigations represent an effort to understand the nature of the metal-metal bond deep within the transition metal series. All three molecules, VCr, NbCr, and VMo, contain 11 valence $(nd+(n+1)s)$ electrons. The ground state in all of these molecules results from a combination of the atoms in their d^4s^1, ^6D(V/Nb)+d^5s^1, ^7S(Cr/Mo) terms, leading to a $1\sigma^2 1\pi^4 1\delta^3 2\sigma^2$ ground configuration. As a result, VCr, NbCr, and VMo all have a $^2\Delta_{5/2}$ ground state and exhibit a formal bond order of 5.5. In addition, the bond lengths in these systems, VCr($r_0=1.726$ Å),[1] NbCr($r_0=1.894$ Å),[1] and VMo($r_0=1.877$ Å),[2] are quite close to the average of their homonuclear counterparts: V_2($r_0=1.776$ Å),[3] Cr_2($r_0=1.686$ Å),[4] Nb_2($r_0=2.079$ Å),[5,6] and Mo_2($r_0=1.940$ Å).[7] These short bond lengths are consistent with the expected formal bond orders of 5 (V_2 and Nb_2), 5.5 (VCr, VMo, and NbCr), and 6 (Cr_2 and Mo_2). From the above values of the bond lengths, along with the previously measured bond lengths of VNb($r_0=1.943$ Å) (Refs. 8 and 9) and CrMo($r_0=1.823$ Å),[10] multiple bonding radii of V, Cr, Nb, and Mo have been derived based on the assumption that the bond lengths in these molecules are the sum of the multiple bonding radii of the constituent transition metal atoms.[2] Using the multiple bonding radii of Nb and Mo, the ground state bond length of NbMo has been predicted to be 2.0149 Å.[2]

As a continuation of our effort to understand the electronic structure and bonding between the group V and VI elements and to test the prediction of the NbMo bond length, R2PI studies of NbMo were undertaken. Theoretical studies of NbMo have not yet been reported, and experimental information is very scarce. A low temperature matrix absorption study by Klotzbücher and Ozin[11] revealed absorption features at 590, 568, 558, and 551 nm, while a Knudsen effusion mass spectrometric investigation by Gupta and Gingerich[12] determined the bond dissociation energy of NbMo to be 4.64±0.26 eV. In this paper we present the results of our spectroscopic investigation of NbMo.

Section II briefly describes the experimental technique employed in this study. Section III presents the spectroscopic results on NbMo. In Sec. IV a discussion of the chemical bonding in this molecule is presented and comparisons to the previously studied related molecules are drawn. Section V concludes the article with a summary of important results from this work.

II. EXPERIMENT

R2PI spectroscopy with time-of-flight mass spectrometric detection was employed to investigate the jet-cooled NbMo diatomic. The molecules were produced by pulsed laser ablation (Nd:YAG, 355 nm, 10–15 mJ/pulse) of a 1:2 molar ratio NbMo alloy disk followed by supersonic expansion in helium carrier gas (160 psi). The resulting jet-cooled molecular beam was roughly collimated by a 1 cm diameter skimmer and allowed to enter the ionization region of a reflection time-of-flight mass spectrometer (TOFMS).[13,14] In this region, the molecular beam was interrogated by first exposing the molecules to radiation produced by a tunable dye laser and subsequently ionizing them with a second laser pulse originating from an excimer laser (KrF, 248 nm, 5.00 eV). The ions were then mass separated in the TOFMS and detected with a microchannel plate detector. Optical spectra were recorded by monitoring the ion signal of the species of interest as a function of the dye laser wave number. Vibronically resolved spectra of the $^{93}Nb^{92}Mo$ (14.8% natural abundance), $^{93}Nb^{95}Mo$(15.9%),

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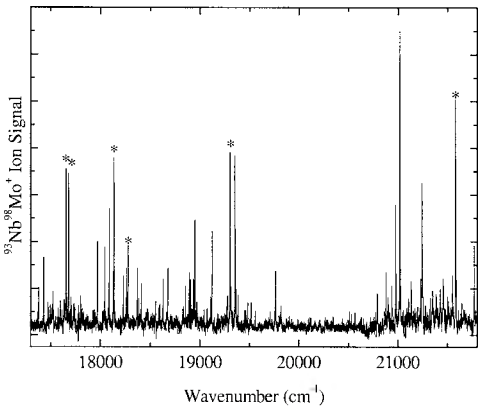

FIG. 1. Vibronically resolved spectrum of $^{93}Nb^{98}Mo$, recorded over the 17 300–21 800 cm^{-1} range. Bands that have been successfully rotationally investigated are indicated by asterisks.

$^{93}Nb^{96}Mo(16.7\%)$, $^{93}Nb^{97}Mo(9.6\%)$, $^{93}Nb^{98}Mo(24.1\%)$, and $^{93}Nb^{100}Mo(9.6\%)$ isotopomers were recorded in the 17 300–22 300 cm^{-1} spectral range. Rotationally resolved spectra (0.04 cm^{-1}) of the more intense features were then obtained by inserting an air-spaced étalon into the grating cavity of the dye laser and pressure scanning using SF_6. An absolute frequency calibration of the rotationally resolved bands below 20 000 cm^{-1} was accomplished by simultaneously recording an absorption spectrum of I_2 and comparing this spectrum to the atlas of Gerstenkorn and Luc.[15,16] For bands above 20 000 cm^{-1}, isotopically pure ^{130}Te was heated to 510 °C to collect the absorption spectrum of $^{130}Te_2$, which was then compared to the atlas of Cariou and Luc[17] to obtain accurate rotational line positions. A Doppler correction was included in the calibration procedure to correct for the frequency shift experienced by the molecules as they travel toward the radiation source at the beam velocity of helium (1.77×10^5 cm/s).

III. RESULTS

The vibronically resolved spectrum of NbMo was recorded using coumarin 540A, 500, 480, 460, and 440 laser radiation for excitation and KrF excimer radiation for ionization. As shown in Fig. 1, several intense isolated vibronic transitions were observed within the 17 300–22 300 cm^{-1} spectral range, but no vibrational progressions could be identified. Among the nine bands that were rotationally resolved, six bands provided satisfactory fits to the standard expression[18]

$$\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1), \tag{3.1}$$

allowing accurate values of the ground state rotational constant, B_0'', to be determined. Table I provides the fitted values of the band origin, ν_0; the upper state rotational constant, B'; and bond length, r', for each band that could be rotationally analyzed. The ground state rotational constant (B_0'') and bond length (r_0'') obtained from a combined fit of all the bands for each isotopomer are provided at the bottom of the table. These bond length values have been obtained by the simple inversion of B_0'' and have not yet been corrected for the ef-

TABLE I. Fitted values of ν_0, B', and r' for each rotationally resolved band of NbMo.

Band type	Parameter	$^{93}Nb^{96}Mo$	$^{93}Nb^{97}Mo$	$^{93}Nb^{98}Mo$	$^{93}Nb^{100}Mo$
$\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})			17 645.5646(35)	
	B' (cm^{-1})	Out of scanned range	Out of scanned range	0.080 946(35)	Out of scanned range
	r' (Å)			2.090 15(45)	
$\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})			17 671.0635(20)	
	B' (cm^{-1})	Out of scanned range	Out of scanned range	0.081 870(28)	Too weak to analyze
	r' (Å)			2.078 32(36)	
$\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})		18 129.5878(37)	18 126.2848(22)	
	B' (cm^{-1})	Mostly outside of scanned range	0.086 249(83)	0.086 189(22)	Badly perturbed and unresolved
	r' (Å)		2.029 95(98)	2.025 58(25)	
$\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})			18 268.5646(119)	
	B' (cm^{-1})	Out of scanned range	Mostly outside of scanned range	0.078 347(27)	Mostly outside of scanned range
	r' (Å)			2.124 53(37)	
$\Omega'=1.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})		19 294.5128(72)	19 294.4202(32)	19 294.2815(48)
	B' (cm^{-1})	Poorly resolved	0.090 803(83)	0.090 609(21)	0.090 841(82)
	r' (Å)		1.978 39(90)	1.975 55(23)	1.963 38(89)
$\Omega'=1.5\leftarrow X\,^2\Delta_{5/2}$	ν_0 (cm^{-1})	21 574.8125(49)		21 572.7564(33)	21 573.6095(25)
	B' (cm^{-1})	0.092 007(110)	Poorly resolved	0.091 602(20)	0.091 870(78)
	r' (Å)	1.970 42(118)		1.964 82(21)	1.952 36(83)
$X\,^2\Delta_{5/2}$	B'' (cm^{-1})	0.088 110(120)	0.087 906(84)	0.087 697(26)	0.087 920(66)
	r'' (Å)	2.013 52(137)	2.010 73(96)	2.008 09(30)	1.995 73(75)

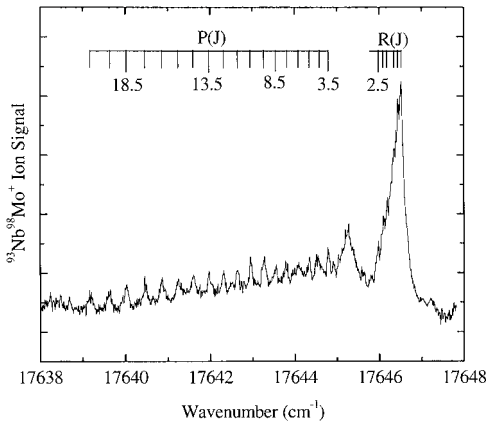

FIG. 2. The 17 646 cm^{-1} $\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$ $v''=0$ band of $^{93}Nb^{98}Mo$.

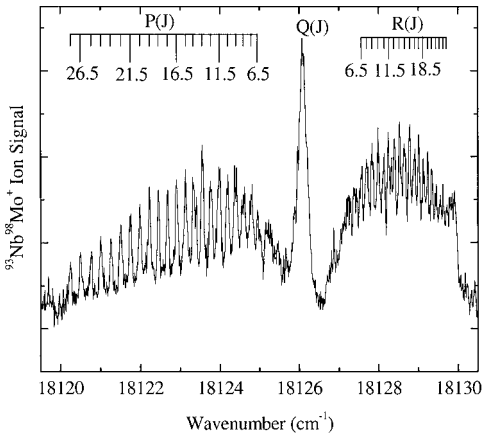

FIG. 3. The 18 126 cm^{-1} $\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$ $v''=0$ band of $^{93}Nb^{98}Mo$.

fects of the spin-uncoupling operator, which couples the $^2\Delta_{5/2}$ ground level with the spin-orbit excited $^2\Delta_{3/2}$ level. These effects are considered in Sec. IV below.

A. The $\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$ band near 17 650 cm^{-1}

Figure 2 displays the rotationally resolved spectrum of the 17 650 cm^{-1} band of $^{93}Nb^{98}Mo$, which overlaps with the absorption feature at 17 605 cm^{-1} that was observed in cryogenic matrices by Klotzbücher and Ozin.[11] The rotationally resolved spectrum is dominated by an intense band head in the R branch, indicating a drop in the rotational constant and an increase in bond length upon excitation. The Q branch is relatively weak and rapidly decreases in intensity with increasing J. A series of P branch lines is observed going off to the red with clearly identifiable lines up to $J''=20.5$. This distribution in spectral intensity among the P, Q, and R branches is characteristic of bands with $\Delta\Omega=0$.[18] Spectral simulation reproduced this intensity pattern for a $\Delta\Omega=0$ transition.

The ground separated atom limit is Nb $4d^45s^1$, $^6D+$Mo$4d^55s^1$, ^7S. The straightforward combination of these terms with maximum pairing of electrons in bonding orbitals is expected to lead to a $1\sigma^21\pi^41\delta^32\sigma^2$ ground electronic configuration, where the numbering of the orbitals is provided based only on the valence $(d+s)$ electrons. The alternative configuration of $1\sigma^21\pi^41\delta^42\sigma^1$ is unlikely because it has an s-electron occupancy of only 1 or 1.5, depending on the extent of sd hybridization in this molecule. The high energy of the d^ns^0 configurations in the separated atoms makes this possibility highly unlikely. Similarly, the alternative configuration of $1\sigma^21\pi^31\delta^42\sigma^2$ may be excluded because of the strong $d\pi$-$d\pi$ bonding character of the 1π orbitals. Therefore, the ground term of NbMo is expected to be $1\sigma^21\pi^41\delta^32\sigma^2$, $^2\Delta$. Further, because the 1δ orbital is more than half full, a $^2\Delta_{5/2}$ ground level is expected. Identification of $P(3.5)$ and $R(2.5)$ as the first lines in the P and R branches confirms the assignment of the above band as an $\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$ transition. A least squares fit of the line positions to Eq. (3.1) provides a good fit of the measured line positions. To obtain the most accurate value of the ground state rotational constant, B_0'', all of the rotationally resolved bands were included in a combined fit, in which the lower state was constrained to have the same value of B'' for all of the measured bands. Fitted values of the upper and lower state rotational constants, $B'=0.080\,946(35)$ cm^{-1} and $B''=0.087\,697(26)$ cm^{-1}, were obtained. These can be inverted to obtain upper and lower state bond lengths of $r'=2.090\,15(45)$ Å and $r_0''=2.008\,09(30)$ Å, respectively.

Line positions for these and all other rotationally resolved bands for all of the interpretable isotopomers of NbMo have been deposited with the Electronic Physics Auxiliary Publication Service of the American Institute of Physics[19] and are also available from one of the authors (Morse). The electronic document also contains spectra for all of the rotationally resolved bands, in addition to the measured line positions.

B. The $\Omega'=2.5\leftarrow{}^2\Delta_{5/2}$ band near 18 126 cm^{-1}

Figure 3 displays a rotationally resolved scan over an isolated band of $^{93}Nb^{98}Mo$ that lies near 18 126 cm^{-1}. It appears likely that this band corresponds to the absorption feature at 18 148 cm^{-1} that was observed in solid argon matrices.[11] This band displays a Q branch that is made intense by overlapping Q lines and nearly symmetrical P and R branches of nearly equal intensities, indicating another $\Delta\Omega=0$ transition.[18] A band head is observed in the R branch at high values of J, indicating that there is a slight increase in the bond length upon excitation. The low J lines in the P and R branches are poorly resolved due to hyperfine splitting caused by the large magnetic moment and large nuclear spin value of ^{93}Nb $(I=9/2)$. However, the hyperfine splitting decreases rapidly with increasing J, allowing the higher J lines in both branches to be clearly resolved, a behavior that is characteristic of the expected Hund's case a_β for a $^2\Delta_{5/2}$ level.[20] Spectral simulation of this band reproduced the above intensity pattern for an $\Omega'=2.5\leftarrow\Omega''=2.5$ excitation. The combined least squares fit of the rotational line positions described above provides $B'=0.086\,189(22)$ cm^{-1}, which corresponds to a bond length of $r'=2.025\,58(25)$ Å. As expected from a cursory examination of the band, this is not much longer than the ground state value of $r_0''=2.008\,09(30)$ Å.

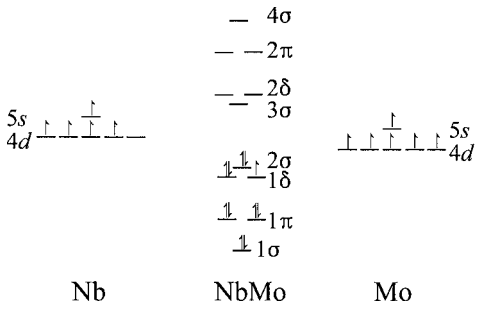

FIG. 4. Schematic molecular orbital diagram of NbMo.

C. Other unassigned bands

A definite assignment of the rotational structure of three isolated bands at 17 970, 19 350, and 21 015 cm^{-1} could not be obtained. The P branch of the first two bands shows clear signs of perturbation by a nearby electronic state. In the 21 015 cm^{-1} band, none of the lines in the P branch could be resolved while only very few high J lines in the R branch could be identified at the available laser linewidth (0.04 cm^{-1}). In these bands rotational lines belonging to only one branch (either P or R) could be identified, providing insufficient data to accurately fit the lines to Eq. (3.1). However, based on the rotational intensity profile, it appears that the bands at 17 970 and 19 350 cm^{-1} probably correspond to $\Omega'=2.5\leftarrow\Omega''=2.5$ transitions while the band at 21 015 cm^{-1} can be tentatively assigned as an $\Omega'=3.5\leftarrow\Omega''=2.5$ excitation.

Bands near 17 671 and 18 268 cm^{-1} could be assigned and fitted as $\Omega'=2.5\leftarrow X\,^2\Delta_{5/2}$ transitions, although in both cases only the $^{93}Nb^{98}Mo$ isotopomer was successfully analyzed. Toward the blue, however, bands near 19 294 and 21 574 cm^{-1} were successfully analyzed as $\Omega'=1.5\leftarrow X\,^2\Delta_{5/2}$ transitions in three different isotopomers of NbMo. Fitted values of the rotational constants and band origins are provided in Table I.

IV. DISCUSSION

The ground electronic configuration of NbMo can be better understood with the aid of the qualitative molecular orbital diagram displayed in Fig. 4. At the separated atom limit, the ground state of Nb is $4d^45s^1(^6D)$ while that of Mo is $4d^55s^1(^7S)$. Therefore, no promotion energy is required to prepare the atoms for bonding. Because the electronegativities and ionization energies of Nb and Mo are similar, when the atoms approach each other from large internuclear distances, a predominantly covalent interaction between the valence orbitals on the two centers splits them into their bonding and antibonding counterparts. In addition, a significant $4d$-$5s$ hybridization is expected. Thus, the 1σ orbital is expected to be a strongly bonding orbital mainly composed of the $4d\sigma+5s\sigma$ hybrid orbitals of Nb and Mo, in which sd hybridization enhances the electron density along the internuclear axis. The 2σ orbital is then expected to be primarily composed of the $4d\sigma$-$5s\sigma$ hybrid orbitals on the two centers, which place most of the electron density off the internuclear axis. The 2σ orbital is probably rather weakly bonding, and it is probably an electron from this orbital that is removed upon ionization to form the ground state of $NbMo^+$. In the closely related molecules V_2 and VNb, there is strong experimental evidence (definitive in the case of V_2) that the analogous $2\sigma_{(g)}$ orbital loses one electron when the molecule is ionized.[8,21] This is computed to be the case in Nb_2 as well[22] and is therefore also expected to occur in NbMo. For this reason, the 2σ orbital is placed slightly above the 1δ orbital in energy. The overlap of $d\pi$ orbitals on the two centers creates a strongly bonding 1π molecular orbital and a strongly antibonding 2π orbital, while the weaker $d\delta$ interaction results in a weakly bonding 1δ molecular orbital and its weakly antibonding 2δ counterpart.

The 11 valence electrons in NbMo are expected to occupy the six bonding molecular orbitals, giving rise to a $1\sigma^21\pi^41\delta^32\sigma^2$ ground electron configuration and a $^2\Delta$ ground term. Two spin-orbit levels derive from the $^2\Delta$ term, $\Omega=5/2$ and 3/2, with Hund's rules predicting a $^2\Delta_{5/2}$ ground level. The results of our rotationally resolved investigations confirm that $\Omega''=5/2$. Therefore, NbMo exhibits a $^2\Delta_{5/2}$ ground state that is analogous to the previously reported mixed group V-VI transition metal diatomics, VCr, NbCr, and VMo.[1,2] Theoretical investigation of the isoelectronic 11 electron system, Nb_2^-, also predicts a $^2\Delta_g$ ground state arising from a predominantly $1\sigma_g^21\pi_u^42\sigma_g^21\delta_g^3$ configuration.[22] This theoretical study supports our ground state assignment for NbMo.

The excited states that obey the electric dipole selection rules, $\Delta\Lambda=0,\pm1$, $\Delta S=0$, and $\Delta\Sigma=0$, which can be readily accessed from the $^2\Delta_{5/2}$ ground state, are $^2\Phi_{7/2}$, $^2\Delta_{5/2}$, and $^2\Pi_{3/2}$. However, in the presence of spin-orbit interaction only Ω remains a good quantum number and many more Hund's case (a) states can be accessed. These include $^4\Delta_{7/2}$, $^4\Delta_{5/2}$, $^4\Delta_{3/2}$, $^4\Phi_{7/2}$, $^4\Phi_{5/2}$, $^4\Phi_{3/2}$, $^4\Pi_{5/2}$, $^4\Pi_{3/2}$, $^2\Delta_{5/2}$, $^2\Delta_{3/2}$, $^2\Phi_{7/2}$, $^2\Phi_{5/2}$, and $^2\Pi_{3/2}$. In the present work, four excited states with $\Omega'=2.5$ and two excited states with $\Omega'=3.5$ have been identified. The congested vibronic spectrum obtained in low resolution suggests that these excited states are significantly mixed due to spin-orbit interactions. This is to be expected given the large values of the atomic spin-orbit parameters, $\zeta_{Nb}(4d)=524$ and $\zeta_{Mo}(4d)=677$ cm^{-1}.[23] Therefore, the $\Omega'=2.5$ states are most likely mixtures of $^2\Delta_{5/2}$, $^4\Delta_{5/2}$, $^2\Phi_{5/2}$, $^4\Phi_{5/2}$, and $^4\Pi_{5/2}$ states; the $\Omega'=1.5$ states are likely mixtures of $^2\Delta_{3/2}$, $^4\Delta_{3/2}$, $^2\Pi_{3/2}$, $^4\Pi_{3/2}$, and $^4\Phi_{3/2}$ states. In any case, the $\Omega'=2.5$ states gain their intensity from the $^2\Delta_{5/2}$ contribution to the upper state, while the $\Omega'=1.5$ states gain their intensity from the $^2\Pi_{3/2}$ contribution. In the absence of identifiable electronic band systems, further speculation about the electronic nature of the upper states is probably futile.

To obtain the most accurate estimate of the ground state bond length in NbMo, we restrict our attention to the most abundant $^{93}Nb^{98}Mo$ isotopomer (24.1%), where we have rotationally resolved the largest number of bands. For this isotopomer, B_0'' is 0.087 697(26) cm^{-1}, based on our combined fit. Simple inversion of this value provides $r_0''=2.008\,09(30)$ Å. However, this B value is really the effective rotational constant for the $^2\Delta_{5/2}$ ground state, which is coupled to the $^2\Delta_{3/2}$ level by the spin-uncoupling operator. Correction for this effect requires that the true B value for the $^2\Delta$ state be obtained using the formula[18]

TABLE II. Multiple bonding radii for V, Cr, Nb, and Mo.

V		Cr	Nb	Mo
0.8912 Å		0.8441 Å	1.0420 Å	0.9729 Å
Molecule	Measured r_0 (Å)	Reference	Fitted r_0 (Å)	Fitted-measured (Å)
V_2	1.7758	25	1.7824	0.0066
VNb	1.9433	9	1.9332	−0.0101
Nb_2	2.0785	5	2.0840	0.0055
VCr	1.7260	1	1.7353	0.0093
VMo	1.8766	2	1.8641	−0.0125
NbCr	1.8939	1	1.8861	−0.0078
NbMo	2.0080	This work	2.0149	0.0069
Cr_2	1.6858	26	1.6882	0.0024
CrMo	1.8231	10	1.8170	−0.0061
Mo_2	1.940	7	1.9458	0.0058

$$B_{\mathrm{eff}}(\Omega) = B_{\mathrm{true}}\left(1 + \frac{2B_{\mathrm{true}}\Sigma}{A\Lambda}\right). \tag{4.1}$$

To estimate this correction, we assume that the partially occupied 1δ set of orbitals have equal compositions on the Nb and Mo atoms, and use the semiempirical method of Ishiguro and Kobori[24] to estimate the spin-orbit parameter, A, as

$$A = -\tfrac{1}{2}[\zeta_{\mathrm{Nb}}(4d) + \zeta_{\mathrm{Mo}}(4d)] = -600.5\ \mathrm{cm}^{-1}. \tag{4.2}$$

Employing this value in Eq. (4.1) then provides B_{true} for $^{93}Nb^{98}Mo$ as $0.087\,703(26)\ \mathrm{cm}^{-1}$, which converts to $r_0''=2.008\,02(30)$ Å. For this molecule, the large A constant combined with the small B value makes the correction for the spin-uncoupling effect rather minor.

In our previous article on the spectroscopy of VMo, we proposed a simple multiple bond radii additivity rule to predict the bond length of NbMo. Using the derived multiple bonding radii values of $r(\mathrm{Nb})=1.0424$ Å and $r(\mathrm{Mo})=0.9725$ Å, the bond length of NbMo was predicted to be 2.0149 Å. The fact that this value lies within 0.007 Å of the measured value clearly validates the idea of multiple bond additivity in the group V-VI set of diatomic transitions. With the value of r_0'' now in hand for NbMo, the set of bond lengths for all of the diatomics composed of V, Cr, Nb, and Mo is complete. A recalculation of the multiple bonding radii, based on the measured r_0'' values, all corrected for the effects of the spin-uncoupling operator, is presented in Table II.

The bond lengths in the group V-VI metal diatomics molecules follow the trend, $r(\mathrm{VCr}) < r(\mathrm{NbCr}) \sim r(\mathrm{VMo}) < r(\mathrm{NbMo})$. This can be explained based on the radial extent of the nd orbitals that dominate the bonding in these species. The radial expectation value, $\langle r_{nd}\rangle$, is much greater for the $4d$ metals than for the $3d$ metals, making the $4d$ orbitals much more accessible for chemical bonding. As a result, $3d$ metals must approach to much shorter internuclear distances to achieve d orbital bonding than is required for the $4d$ metals. Accordingly, the optimal bond length in a $3d$ transition metal diatomic like VCr is much smaller than that in a $4d$ diatomic like NbMo. Nevertheless, in all examples of group V and VI diatomic metals, the short bond lengths demonstrate that the bonding in these molecules is dominated by the d electrons. When one of the atoms in VCr is replaced by a $4d$ metal (Nb or Mo), the nature of bonding is intermediate between VCr and NbMo, as is reflected in the bond lengths.

V. CONCLUSION

The vibronic spectrum of NbMo has been recorded in the $17\,300$–$22\,300\ \mathrm{cm}^{-1}$ region using the resonant two-photon ionization technique. The spectrum is quite dense, and no electronic band systems have been identified. Four excited vibronic levels with $\Omega'=2.5$ and two with $\Omega'=3.5$ have been identified. Rotational resolution of these bands confirms that the ground state of NbMo is of $^2\Delta_{5/2}$ symmetry, resulting from a $1\sigma^2 1\pi^4 1\delta^3 2\sigma^2$ configuration. The best estimate of the ground state bond length is $r_0''=2.008\,02(30)$ Å. This agrees very well with the predicted value of $r_0=2.0149$ Å, which was previously obtained from multiple bond radii for the V, Cr, Nb, and Mo atoms that were obtained from studies of other transition metal diatomics.

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